

# Bulletin of the Agricultural Chemical Society of Japan.

## TRANSACTIONS

### Note on the Determination of Fusel Oil with Vanilline-Sulphuric Acid Reagent.

By Masakazu YAMADA and Katuitiro TAKAKISI.

The Governmental Institute of Brewing, Takenogawa, Tokyo.

(Received May 28, 1938.)

As to the determination of fusel oil in beverages, Komarowski's colorimetric method with aromatic aldehyde and sulphuric acid has been in use as the simplest and especially Takahasi's method with vanilline in place of original salicylic aldehyde was decided to be the most convenient.

But in this case the care indicated by Bleyer and his coworkers must also be taken, for the color-depths caused by different alcohols are diverse as follows:—

Figures show color-depth.

reagent	alcohol	iso-propyl	n-propyl	iso-butyl	n-butyl	iso-amyl	Color	
Vanilline + $H_2SO_4$		0.1	0.1	2.5	0.1	1	red	Yamada
p-Dimethyl aminobenzald. + $H_2SO_4$		—	0.24	1.7	—	1	orange	Bleyer
		0.1	0.1	1.0	0.1	1	reddish	Yamada
p-Oxybenzald. + $H_2SO_4$		0.05	0.05	2.5	0.05	1	violet	Yamada
Salicylaldehyde + $H_2SO_4$		—	0.1	3.0	—	1	violet	Bleyer

In all cases the color shows the deepest with isobutylalcohol but quite faint with alcohols of normal type. Fortunately fusel oil consists mainly of isoamylalcohol and so the large error may be avoided when that alcohol is chosen as the control.

Procedure: To 1 cc of distillate add 2 cc of 0.5% vanilline solution in conc. sulphuric acid and shake. Warm in the boiling water-bath for 3 minutes. Add 1 cc of water and shake. Observe reddish violet color developed after half an hour.

Control solution: 1% isoamylalcohol in 15% ethylalcohol.



## A New Aging Method of Saké.

By Masakazu YAMADA, Katuitiro TAKAKISI  
and Tokuro TANABÉ.

The Governmental Institute of Brewing, Takinogawa, Tokyo.

(Received May 28, 1938.)

Saké is usually brewed in winter utilizing low temperature and after various treatments of compressing, settling and pasteurization, it is stored for several months and then drunk.

Often want of aged saké in spring should be filled up with fresh saké quickly matured and so a few aging method have been devised. Thus electric current, ozone gas or specially devised vessels with chips of cryptomeria timber were applied, but sure effects have not yet been attained.

Now sugar content in saké indicates minimum at compressing period but then gradually increases until pasteurization. This is due to the action of diastatic enzyme extracted in the fluid, which converts degraded dextrin into sugar. Other enzymes will also be active until this stage, for aging phenomena progresses quite energetically. Increase of sugar is first ceased by pasteurization where heating at  $50\sim 55^{\circ}$  is prevailed and this fact shows the destruction of diastatic enzyme. It is quite curious that koji-diastase is destroyed at  $45\sim 50^{\circ}$  far lower from its optimum temperature  $55^{\circ}$ , but now it became clear that this was due to the act of alcohol, which existed ordinarily over 15% in saké. So if quick aging is required, it may easily be attained by shortening of settling period with heating. 2~3 weeks at  $15\sim 25^{\circ}$  instead of usual 35~40 days at  $6\sim 10^{\circ}$  are the most efficient conditions. Then saké is pasteurized at  $50\sim 55^{\circ}$ , and kept in cryptomeria barrel only for 2 weeks. Here aged saké is completed.

### EXPERIMENTAL.

I. The change of the constituents of saké in various stages of brewing. (Figures show average of 11 samples)

	Sp. gr	alcohol % (Vol.)	total acid %	extract %	sugar %	dextrin %
Compressing >ca. 20 days	0.9991	17.14	0.1527	5.437	1.136	2.580
Settling stage >ca. 20 days	0.9992	16.74	—	—	1.960	—
Pasteurization	0.9994	16.61	0.1450	5.385	2.657	1.239
ca. 2 months after pasteurization	0.9996	16.48	0.1426	5.212	2.698	1.190

II. The destruction of diastatic enzyme by pasteurization.

Figures indicate diastatic power d—the volume of 0.1 percent starch solution



that would be converted to erythrodextrin by 1 cc of the enzyme solution (saké) in 30 minutes.

Each heating for 15 minutes.

saké	before-heating	heating at 30°	heating at 40°	heating at 45°	heating at 47°	heating at 50°
No. 7	10	10	10	2.0	0.071	0
No. 9	6.6	6.6	4.0	0.71	0.083	0
No. 10	2.5	2.2	1.7	0.55	0.055	0

III. The influence of the temperature and alcohol content upon the diastatic power of koji-diastase.

Enzyme solution: 50 g of koji was extracted with 250 cc of water at 13° for 4 hours and filtered. To the filtrates were added alcohol and water, so as to the resultant solutions contained each 0~30% of alcohol and showed half diastatic activity of original filtrate. Diastatic powers of such enzyme solutions:—

alcohol content of enzyme solution	heated at 52~54° for 15 min.	heated at 52~54° for 6 hours	alcohol content of enzyme solution	heated at 52~54° for 15 min.	heated at 52~54° for 6 hours
0%	6.7	—	20%	2.0	0
5%	6.7	6.7	30%	1.0	0
10%	6.7	3.0	0%	6.7 (not heated)	—
15%	4.0	0			

IV. Experiment of quick aging.

Samples of saké were stored in bottles at designed temperatures and sugar contents were determined.

Saké	storage temp.	the 1st day	after 10 days	after 20 days	after 30 days
A	22°	3.07%	3.61%	4.21%	—%
	15°	3.07	3.26	4.03	4.11
	6°	3.07	3.14	3.59	3.66
B	22°	1.65	2.86	3.40	3.53
	15°	1.65	2.24	2.70	2.84
	6°	1.65	1.99	2.30	2.56
C	22°	2.82	4.17	4.25	4.41
	15°	2.82	3.83	4.08	4.13
	6°	2.82	3.31	3.60	3.71



## On an Irritant Smell of Saké changed in Quality.

By Masakazu YAMADA and Tatuo URANO.

The Governmental Institute of Brewing, Takinogawa, Tokyo.

(Received May 28, 1938.)

The barrelled saké often indicates a strong wood-odor of cryptomeria and at the same time irritant smell of acetic acid along with or without odor of ethylacetate. In that case generally the taste becomes sour. Analytical data of such samples are following:—

Saké	Sp. gr.	alcohol	total acid	remarks
A (Unchanged original saké)	0.9966	17.7%	0.1623%	
B (To A was added 20% of water and barrelled.)	1.0035	12.5	0.1770	odor of ethylacetate
C	—	12.5	0.3240	odor of acetic acid and ethylacetate
D	1.0056	12.4	0.2299	odor of acetic acid
E	1.0091	9.2	1.2038	odor of acetic acid and ester

B~E Changed in quality.

All samples contain less than ca. 13% of alcohol and a large quantity of acid, the main part of which being acetic acid. (Usually saké contains 15~18% of alcohol and 0.1~0.2 of total acid.)

Turbidity was not caused by bacteria but some wild yeast (*Willia* sp.) which was able to form ethylacetate.

The same result is often obtained when 5~10% alcohol solution is oxidized with chips of cryptomeria timber. In this case ordinarily acetaldehyde should be produced as an end product while existence of wild yeast brings the reaction farther to acid or ester.

5% alcohol solution with 18 g of cryptomeria timber				10% alcohol solution with 18 g of cryptomeria timber		
	Aldehyde	Total acid as acetic	Remarks	Aldehyde	Total acid as acetic	Remarks
Original solution	0.00157%	0 %		0.00313%	0 %	
After 15 days	0.03118	—		0.00440	—	
" 23 "	0.05019	0.0060	<i>Willia</i> appeared	0.01233	0.3680	<i>Willia</i> appeared
" 41 "		0.0300			0.6608	
" 216 "		0.0826	Odor of ester		2.3674	No bacteria
" 284 "		—			*3.0029	

\* Silver salt prepared contained 64.88% of Ag. (Calc. from  $C_2H_3O_2Ag$ : 64.64%) Consequently, the phenomena comes from too much addition of water to saké and incomplete sterilization of the barrel. The latter cause is easily prevented by washing the barrel with 0.1% of hydrogen-peroxide solution.



## On the Destruction of 'Hioti' Smell by Hydrogen Peroxide.

By Masakazu YAMADA and Hisao MATUI.

The Governmental Institute of Brewing, Takinogawa, Tokyo.

(Received May 28, 1938.)

The displeased 'hioti'-smell of putrefied saké is so persistent that it has difficultly been removed by various treatments. Hither-to, the filtration after adding of fresh saké-cake, the adsorption with active carbon or the aeration etc. were practiced but no remarkable effects were attained.

Yukio Tomiyasu found an interesting fact that diacetyl was the main component of 'hioti'-smell and partly succeeded to remove the smell by adding neutralized hydroxylamine-hydrochloride solution to putrefied saké. In that case, the reagent combines diacetyl, forming odorless dimethyl-glyoxime. Lately one of the present authors found that the putrefaction of saké was usually accompanied with the increase of ketones of four carbon atoms. These are diacetyl and especially acetoin.

The contents of such substances vary as follows:—

1. To 3.5 l of saké was added 3 drops of putrefied saké and incubated at 25°.

	Days after incubation	Diacetyl	Acetoin	2,3 butylen-glycol	Remarks
Original saké	1	0.000072%	0.000628%	0.03782%	
Putrefied saké	10	0.000507	0.006556	—	Slightly turbid
"	18	0.000769	0.001389	0.04685	Turbid
"	26	—	0.002013	0.04049	

2. To 5 l of saké was added 10 drops of putrefied saké and incubated at 29°.

Days after inoculation	Total acetoin (Diacetyl and acetoin as acetoin)	Turbidity by bacteria
Original saké	0.000366%	
2 days	0.002654	
4	0.004514	Slightly cloudy
5	0.004697	Cloudy
9	0.006161	Turbid +
10	0.007991	++
11	0.009100	+++
12	0.006588	Translucent
13	0.004148	
14	0.004206	
15	0.004575	Diacetyl 0.000942%

Within the present authors' attempts to destroy the displeased smell, hydrogen-peroxide was concluded to be the most efficient and applicable. When man adds one-thousandth part of ca. 35% hydrogen-peroxide solution to putrefied saké and stands for 5~7 days, the indisposed smell may be completely removed.

In the case diacetyl was perceived to have been decomposed to acetic acid as J. Boeseken's report (*Recueil des Travaux Chimiques des Pays-Bas et de la Belgique* Tome 30. 141. 1911.) but no remarkable increase of acid was occurred, because even putrefied saké contained only a minute quantity of diacetyl.

Addendum: If acetoin is added to cold Fehling's solution, reduction of copper preceeds to form the metallic copper (copper mirror).

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The contents of such substances vary as follows:—

1. To 3.5% of saké was added 3 drops of putrefied saké and incubated at

Days after incubation	Diacetyl	Acetoin	Remarks
Original saké	0.000072%	0.000032%	
Putrefied saké	0.000297	0.000250	Slightly turbid
10	0.000780	0.001289	Turbid
20	0.002012	0.003012	

Days after incubation	(Diacetyl and acetoin in acetoin)	Infinitely by acetoin
Original saké	0.0003662%	
2 days	0.002054	
4	0.004519	Slightly cloudy
6	0.004697	Cloudy
8	0.006161	Turbid +
10	0.007391	
11	0.009700	
12	0.008288	Translucent
13	0.004148	
14	0.0041208	
15	0.003252	



## ABSTRACTS

from

## TRANSACTIONS published in JAPANESE

(Pages refer to the Japanese originals of this volume unless otherwise noticed)

**On the Optical Properties of the Fermentation  
Lactic Acids. Part VI.**

On some Properties of Racemiasse.

(pp. 645~649)

By Hideo KATAGIRI and Kakuo KITAHARA.

(Agr. Chemical Laboratory, Kyoto Imperial University. Received Apr. 20, 1938.)

It was found that Racemiasse was very sensitive to acid; any racemization was not revealed at pH=4, while the optimum pH value was observed to be 6~8.

Irreversible inactivation of Racemiasse was observed when the resting cells of *L. plantarum* were kept at room temperature, however the aqueous or glycerol suspension of the bacteria could be kept for ten days in an ice chamber, without any noticeable destruction of Racemiasse. The dried bacteria obtained by dehydration on sulphuric acid at 2~4°, revealed remarkable racemization, while Racemiasse was completely destroyed when the bacteria were dehydrated by acetone or alcohol-ether.

Any experimental proof for the nature of Racemiasse observed by Tatum, Peterson and Fred [Biochem. J., 30, 1892 (1936)] who concluded that Racemiasse was composed of a soluble, heat-labile enzyme and of an insoluble, heat-stable coenzyme, was not obtained with *L. plantarum*. The fermented liquid of the bacteria was not revealed any noticeable racemization nor any acceleration for racemization with thoroughly washed bacterial cells.

Any racemization of lactic acid anhydride, ethyl lactate, alanine, phospholactic, mandelic, malic and tartaric acids was never observed by Racemiasse, while selective decomposition of *dl*-malic acid was pointed out by *L. plantarum* with which presence of Fumarase was ascertained.

**On the Hydrolytic Decomposition Products of the  
Mucilaginous Substance of Yam.**

(Dioscorea Batatas, Decne.)

(pp. 650~658)

By Teizo TAKAHASHI.

(Agri. College, Gifu, Japan. Received Apr. 18, 1938.)

The mucilaginous sub<sub>t</sub>. of yam was hydrolysed and the following amino acids were isolated.

Glycocoll	—%	Valine	1.04%	Lysine	0.89%
Proline	3.74	Aspartic acid	2.50	*Cystine	1.26
Serine	0.04	Glutamic acid	5.49	*Tryptophane	2.26
Leucine	2.60	Arginine	1.57		
Isoleucine	1.40	Histidine	0.85		

\*.....Colorimetric.

Leucine was isolated as *d*, *l*-leucine.

### On Yeasts from Apples.

(pp. 659~670)

By Tosinobu ASAI.

(Agricultural Chemical Laboratory, Morioka Agricultural College, Japan.

Received Mar. 9, 1938.)

### On the Content of 0.2 N HCl Soluble Potash in Tyosen Soils. (I)

(pp. 671~685)

By Dr. MISU Hideo.

(Agricultural Experiment Station Government General of Tyosen.)

### Chemical Studies on the Fluorescence of the Color in Sake.

(pp. 686~688)

By Tetutaro TADOKORO, Tuneyuki SAITO and Keizo ITO.

(Hokkaido Imperial University, Japan. Received Apr. 30, 1938.)

### Feeding Experiments with Amino Acid Mixture. I.

Synthesis and Physiological Significance of

$\alpha$ -Amino- $\beta$ -oxy-Butyric Acid.

(pp. 689~696)

By Siro MAEDA, Tuneto HIGASHI and Hitosi MATUOKA.

(The Institute of Physical and Chemical Research. Received June 30, 1937.)

### Chemical Studies on Japanese Coccidae. (XIX)

Nitrogenous and Inorganic Substances of

*Tachardina theae* Green et Mann.

(pp. 697~701)

By M. KAWANO and R. MARUYAMA.

(Laboratory of Ohsaka Factory of Sankyo Co. Ltd., Received May 9, 1938.)



### On the Inorganic Constituents of Green-Manure Crops. III.

(pp. 702~708)

By K. KONISHI and T. TSUGE.

(College of Agriculture, Kyoto Imperial University. Received May 14, 1938.)

#### Phosphoric acid contents of nodules and roots, and lime contents of nodules.

The amounts of  $P_2O_5$  and CaO in root nodules from several leguminous crops were determined by measuring microphotometer curves as demonstrated in the authors' paper (Bulletin of the Agr. Chem. Soc. Japan vol. 13, no. 3, 1937). It was evidenced that ashes of roots from alfalfa plant was quantitatively higher in phosphoric acid than those of nodules, while those of nodules from soybean, lupine and serradella were lower than of their roots. The lime contents of nodules from "genge", saatwicken and field pea exceeded those of their roots amounting 10.0, 7.40 and 11.3 per cent respectively.

Either the increased supplies of  $K_2HPO_4$  or  $CaCO_3$  to soybean seedling on sand cultures seemed negligible factors affecting the contents of  $P_2O_5$  in ashes of their nodules, but a striking relationship between the Ca content of nodules and the  $CaCO_3$  supply.

### Blätteralkohol. I. Mitteilung.

Vorkommen von Blätteralkohol im Pflanzenreich.

(ss. 709~716)

Von Sankiti TAKEI, Yajiro SAKATO, Minoru ŌNO und Yosiro KUROIWA.

(Aus. d. Agrikulturchem. Laborat. d. Universität Kyoto. Eingegangen am 25. April, 1938.)

Wie bekannt, riecht das im Pflanzenreich häufig vorkommende Blätteraldehyd (Hexen-2-al-1 oder  $\alpha$ ,  $\beta$ -Hexenal)<sup>(1)</sup> beim Verdünnen nach grünem Gras sowie auch nach grünen Blättern. Wir haben nun aus grünen Blättern verschiedener Pflanzen durch Wasserdampfdestillation Blätteröl gewonnen, welchem wir Hexen-3-ol-1 ( $\beta$ ,  $\gamma$ -Hexenol) und Hexen-2-al-1 ( $\alpha$ ,  $\beta$ -Hexenal) als krystallinische Derivate entzogen. Unseren mehrfachen Versuchen zufolge wurde in den Blätterölen ausnahmslos viel mehr Hexen-3-ol-1 als Hexen-2-al-1 festgestellt, zwar bildete ersteres den wichtigsten Bestandteil des grünlichen Geruches. Hiernach möchten wir diesen interessanten pflanzlichen Alkohol von jetzt an bequemlichkeitshalber als "Blätteralkohol" bezeichnen.

Dieser Blätteralkohol kommt im Pflanzenreich fast immer in freiem Zustande vor, als einzige Ausnahme findet er sich gebunden in japanischem Pfefferminzöl in Form von Phenylessigester,<sup>(2)</sup> wo er zwiebelartig riecht. Synthetisch kann man aus Sorbinsäureäthylester durch Bouveaultsche-Reduktion ein Hexen-3-ol-1 ge-

(1) Th. Crutius u. H. Franzen: A. 390, 89~121 (1912); 404, 93~130 (1914).

(2) H. Walbaum: C. 1918 II, 25.



winnen,<sup>(3)</sup> dieses zeigt jedoch gar keinen Geruch von grünen Blättern. Nach unserer Anschauung<sup>(3)</sup> bildet das synth. Hexen-3-ol-1 ein Raum-Isomer von natürl. Blätteralkohol, d. h. das synth. Hexen-3-ol-1 gehört zur *cis*-Form und der Blätteralkohol zur *trans*-Form. Ausser durch den verschiedenen Geruch lassen sich die beiden Hexen-3-ol-1 leicht durch das Merkmal verschiedenen Schmelzpunktes der ihnen entsprechenden Derivate chemisch unterscheiden.

	natürl. Blätteralkohol ( <i>trans</i> -Hexen-3-ol-1)	synth. Hexen-3-ol-1 ( <i>cis</i> -Hexen-3-ol-1)
4'-Joddiphenylurethan	157°	148°
3,5-Dinitrobenzoat	49°	28°
Phthalestersäures-Silber	126°	118°
Allophanat	146°	143°
Anthrachinon- $\beta$ -carbonat	68°	50°

Nach unseren Erfahrungen besteht auch eine leichthandliche Methode zur Identifizierung des Blätteralkohols darin, dass man eine kleine Menge Substanz (ca. 0.1 g) mittels Chromtrioxyd in Blätteraldehyd oxydiert und es in gut krystallisierbares 2,4-Dinitrophenylhydrazon (Schmp. 144°) sowie Semicarbazon (Schmp. 173°) überführt.

Auf diese Weise vermochten wir in den grünen Blättern nachstehender Pflanzen Blätteralkohol sowie Blätteraldehyd nachzuweisen:

Tee (*Thea sinensis*), Efeu (*Parthenocissus*), Fallnetz (*Fatsia japonica*), Klee (*Trifolium repens*), Eiche (*Quercus glauca*), Weizen (*Triticum vulgare*), Robinie (*Robinia pseudo-acacia*), Maulbeer (*Morus bombycis*), Rettich (*Raphanus sativus*), *Eurya japonica*, *Pieris japonica*.

## Blätteralkohol. II. Mitteilung<sup>(1)</sup>

Einige aus Blätteralkohol synthetisch gewonnene Riechstoffe.

(ss. 717~723)

Von Sankiti TAKEI, Minoru ÔNO, Yosirô KUROIWA,

Tosio TAKAHATA und Tuneo SIMA.

(Aus d. Agrikulturchem. Laborat, d. Universität Kyoto, Eingegangen am 25. April, 1938)

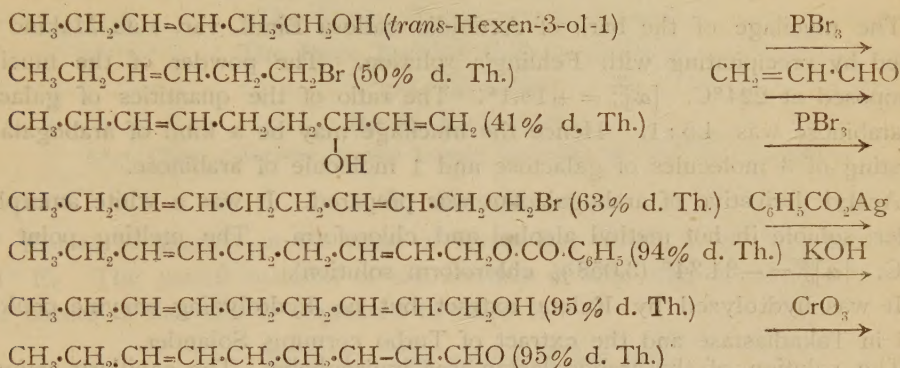
Es ist beachtenswert, dass aus dem im Pflanzenreich viel verbreiteten Blätteralkohol<sup>(1)</sup> auch chemisch einige wichtige Riechstoffe hergestellt werden konnten. Treff und Werner<sup>(2)</sup> haben aus natürl. Blätteralkohol synthetisch Jasmon gewonnen, das den wichtigsten spezifischen Geruchsbestandteil des Jasminblütenöls ausmacht. Ruzicka und Schinz<sup>(3)</sup> konnten von synth. gewonnenem *cis*-Hexen-3-ol-1<sup>(1)</sup> — dem Raum-Isomer des Blätteralkohols — ausgehend, das Veilchenblätteraldehyd, nämlich das Nonadien-2,6-al-1, herstellen und seine Identität mit dem aus Veilchenblättern extrahierten Stoff durch Vergleich des Schmelzpunktes beider Semicarbazone (Schmp. 168~8°) konstatieren.

Nach unserer Annahme müssen das natürl. Veilchenblätteraldehyd zum 2-*trans*-6-*trans*-Nonadienal-1 dagegen der von Ruzicka und Schinz künstlich aus

(3) S. Takei, T. Imaki u. Y. Tada: B, 68, 953 (1935).



synth. *cis*-Hexen-3-ol-1 erhaltene Stoff zum 2-*trans*-6-*cis*-Nonadienal-1 gehören<sup>(1, 4)</sup>. Geht man aber statt von dem *cis*-Hexen-3-ol-1 von dem Blätteralkohol, dem *trans*-Hexen-3-ol-1 aus, so muss man das 2-*trans*-6-*trans*-Nonadienal-1 erhalten. Auf Grund dieser Überlegung haben wir auf folgende Weise 2-*trans*-6-*trans*-Nonadienal-1, d. h. natürl. Veilchenblätteraldehyd, in guter Ausbeute gewonnen.



Das Endprodukt besitzt einen an den Saft frischer Gurken erinnernden Geruch<sup>(5)</sup> und ergibt leicht Semicarbazon (Schmp. 157.5°) sowie 2,4-Dinitrophenylhydrazon (Schmp. 113°).

Nonadien-1,6-ol-3 und Nonadien-2,6-ol-1, die Zwischenprodukte bei dieser Synthese, riechen nach Zypressenblättern bzw. nach Seegurken. Das aus Önanthol und Äthyljodid erhaltene Nonanol-3 zeigt einen eigentümlichen Holzgeruch oder den Japanlack-Geruch. Die Schmelzpunkte der krystall. Derivate dieser C<sub>9</sub>-Alkohol sind:

	4'-Joddiphenylurethan	Allophanat
Nonadien-1,6-ol-3	122°	125°
Nonadien-2,6-ol-1	137°	140°
Nonen-6-ol-3	110°	96°
Nonanol-3	146°	135°

(1) I. Mitteilung: J. Agr. Chem. Soc., **14**, 709 (1938).

(2) W. Treff und H. Werner: B., **83**, 640 (1935).

(3) L. Ruzicka u. H. Schinz: Helv, **16**, 1592, 1602 (1934).

(4) vergl. B. Greby: C., **1937** I, 1405.

(5) E. Späth u. Kessler: C., **67**, 1499 (1934).

## Untersuchungen über die Herstellungsmethode des Bagasse-Zellstoffes.

(1). Über den Bagasse-Zellstoff nach dem Natronverfahren.

(ss. 724~732)

Von Syosuke TANAKA und Muneo KOORIYAMA.

(The Department of Industry, Government Reserch Institute, Taiwan, Japan,

Eingegangen am 2. Apr. 1938.)



## The Chemical Constituents of *Actinidia Callosa*

### Lindl. var. *Rufa* Makino. II.

(pp. 733~736)

By Yoshijiro KIHARA.

(Agr. Chem. Lab., Tokyo Imperial University, Received Apr. 20, 1938.)

The mucilage of the bark of *Actinidia callosa* Lindl. var. *rufa* Makino was purified by precipitating with Fehling's solution. The powder of the mucilage decomposed at 224°C.  $[\alpha]_D^{20} = +15.1^\circ$ . The ratio of the quantities of galactose and arabinose was 4.5:1. Hence the mucilage may be a kind of arabogalactan consisting of 3 molecules of galactose and 1 molecule of arabinose.

Acetyl derivative of arabogalactan was prepared. It was a white amorphous powder, soluble in hot methyl alcohol and chloroform. The melting point was 216°C.  $[\alpha]_D^{18} = -34.34^\circ$  (3.058% chloroform solution).

It was hydrolyzed by Eulota extract but no hydrolyzing enzyme could be found in Takadiastase and the extract of *Turbo cornutus* Solander.

The solution of the arabogalactan was hydrophobe. The capillary action of the dilute solution was estimated by the penetration velocity through filter paper.

Glucomannan of *Narcissus Tazetta* and the mucilage of *Abelmoschus manihot* were also hydrophobe as well as the arabogalactan, while soluble starch was hydrophile. Three % solution of the arabogalactan was a viscous jelly. The viscosity decreased rapidly when it was diluted to 2%.

The insoluble pentosan of the bark had previously reported as *Nashikazura* araban. It was hydrolyzed by boiling with 1%  $H_2SO_4$  for 4 hours. The hydrolysate was neutralized with  $BaCO_3$  and then  $BaSO_4$  precipitated was removed by the filtration. The filtrate was concentrated under diminished pressure and an equal volume of alcohol was added. A white precipitate of Ba compound was obtained. It gave a remarkable uronic acid reaction with naphthoresorcin.

The quantity of uronic acid was estimated by the Dickson, Otterson and Link's method.

The molecular ratio of arabinose and hexuronic acid was 4:3. The *Nashikazura* araban may be a kind of polysaccharide consisting of 4 molecules of arabinose and 3 molecules of hexuronic acid. It was precipitated from the aqueous solution with  $Ba(OH)_2$ ,  $CuSO_4$  and Fehling's soln. The aqueous solution was acidic and dextro-rotatory.

The alcohol soluble carbohydrates of the fruits of *Actinidia callosa* Lindl. consisted of reducing sugar only. The solution of reducing sugar showed  $[\alpha]_D^{20} = -35.3^\circ$ . It gave glucosazone and Seliwanoff reaction. It may be inverted from sucrose during the sampling.

The cold water soluble carbohydrates of the fruits was precipitated by the addition of alcohol.

It was a kind of polysaccharide consisting of 1 molecule of hexose and 1 molecule of pentose.



The solution was precipitated by  $\text{CuSO}_4$  and Fehling's solution, but  $\text{Ba(OH)}_2$ . A phenylosazone melting at  $185^\circ\text{C}$  was prepared from the hydrolysate.

The hot water soluble fraction of the fruits showed the reaction of pectin.

### On the Soil Type in Manchuria (Part II).

The Brown Forest Soil in Koroto.

The Basic Reddish Soil in Yohakuji.

(pp. 737~742)

By R. KAWASHIMA.

(Agr. Chem. Laboratory, Kyushu Imperial University, Received Apr. 27, 1938.)

### I. Koroto

Koroto is situated on the coast of Ryoto bay nearly in lat.  $41^\circ\text{N}$ . and long.  $121^\circ\text{E}$ . The parent material of soil consists of clay slate of cambro-ordovician. The nature of fine soil is expressed in table I.

Table I. The nature of fine soil.

Layer	Thick- ness cm	Clay ( $<10\mu$ ) %	Clay ( $<1\mu$ ) %	N %	pH		Daiku- hara acidity ( $y_1 \times 3$ )	Hydroly. acidity ( $y_1$ )	Ex- change capacity (m. eq.)	Ex- change- able Ca. (m. eq.)	% of Ca
					$\text{H}_2\text{O}$	KCl					
A	35	24.37	6.70	0.08	6.63	5.32	0.4	4.6	8.42	5.74	68.2
B	50	48.69	28.03	0.05	5.00	3.78	56.3	21.8	18.03	2.76	15.3

As in the table, translocation of clay particles from the surface layer are demonstrated. The small content of nitrogen indicates the scarcity of humus. The weakness of acid reaction and fairly high calcium saturation in A-layer is due to the influence of herbaceous vegetation after the loss of forest. The acid reaction in B-layer is much more stronger than A, and its exchange complex is exceedingly deficient in lime.

The colloidal clay below  $1\mu$  in diameter were separated and analysed. The analytical data are as follows.

Table II. The composition of colloidal clay.

Layer	Exchange capacity (m. eq.)	Loss on ignition %	$\text{SiO}_2$ %	$\text{Al}_2\text{O}_3$ %	$\text{Fe}_2\text{O}_3$ %	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$
A	41.76	14.49	45.40	21.19	9.82	3.63	2.80	0.30
B	45.52	11.56	45.42	23.15	11.37	3.33	2.53	0.31

As in table II, there is observed a slight accumulation of sesquioxides in colloidal clay of B-layer. It is regarded that this brown forest soil wear in some measure an aspect of reddish acid soil type in wet and hot climate.



## II. Yohakuji

Yohakuji is situated about 150 km distant to north-west from Koroto. The parent material of soil consists of gneiss. The soil reacts basic and effervesces strongly on addition of acid. Although there remain in profile some clear morphological characteristics as brown forest soil, it changed secondarily to such basic and calcareous state, owing to the influence of deforestation in remote past. The climatical data are not available, but it is certain that the evaporation is much greater than the precipitation. The nature of soil are indicated in following two analytical results.

Table III. The properties of fine soil.

Layer	Thick- ness (cm)	Clay ( $<10\mu$ ) %	Clay ( $<1\mu$ ) %	N %	pH		Water soluble		Exchange capacity (m. eq.)
					H <sub>2</sub> O	KCl	Cl %	SO <sub>3</sub> %	
A	40	26.01	5.20	0.07	8.23	7.48	0.276	0	15.49
B <sub>1</sub>	70	35.24	11.36	0.05	8.14	7.29	0.149	0	17.00
B <sub>2</sub>	60	33.71	8.12	0.04	8.04	7.17	0.236	0	21.14

Table IV. The composition of colloidal clay.

Layer	Exchange capacity (m. eq.)	Loss on ignition %	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$
A	52.12	18.64	37.47	15.34	8.43	4.14	3.06	0.35
B <sub>1</sub>	57.04	14.08	42.12	23.58	9.73	3.03	2.39	0.26
B <sub>2</sub>	56.13	13.54	42.53	19.84	10.88	3.63	2.69	0.35

### Some New Ingredients of Brown Algae\*, VII.

On the unsaponifiable Liquid Part of the Algae Fats.

(pp. 743~748)

By K. SHIRAHAMA.

(Hokkaido Imperial University, Received May 1, 1938.)

A liquid part obtained from *Alaria crassifolia* Kjellm. after excluding pelvesterol, was separated to three fractions by solvents.

I. 80% methanol soluble fraction (19% of the total liquid substance) had a narcotic action and activates the action of lipase as already reported. Its distilled part (120~140°C, 3 mm) had distinctly stronger actions, and (Iodine value 147) produced a small amount of crystall (m.p. 149°C) having the empirical formula C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>, but showed physiological actions above mentioned.

II. 90% methanol soluble substance (31% of the total liquid substance) contains vitamine A, and

III. Petroleum ether soluble substance (50% of the total liquid) has chiefly composed of hydrocarbon C<sub>18</sub>H<sub>36</sub> and several others such as C<sub>20</sub>H<sub>34</sub>, C<sub>21</sub>H<sub>38</sub> and higher unsaturated terpenes, but contained no squarene.

\* This subject is continued from preceding reports entitled "On the Unsaponifiable Matter of the Algae Fats."